

Short communication

Molybdenum-oxygen anionic chain grafted by Cu-phen complex. Synthesis, crystal structure and properties



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ABSTRACT

An unreported inorganic-organic hybrid compound $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2(\text{Mo}_3\text{O}_{10})]$ (**1**) was hydrothermally synthesized and characterized with elemental analysis, IR spectroscopy, thermal analysis, luminescent spectroscopy, magnetic measurement. The crystal structure was determined with X-ray single-crystal diffraction. Compound **1** has a 1-D chain structure constructed by $\{\text{Mo}_3\text{O}_{10}\}^{2-}$ units via edge-sharing and $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2]^{2+}$ fragments grafting the chain from two sides via the coordination of the terminal oxygen atom of the MoO_6 octahedra to Cu^{2+} ion. The coordination of phen to Cu^{2+} ion increases the molecular rigidity so that an emission peak at 500 nm was observed and assigned to the phosphorescent $n-\pi^*$ and $\pi-\pi^*$ transition from ligand-centered triple state. In compound **1** Cu(II) exhibits an antiferromagnetic exchange.

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Molybdate anions undergoes a polymerization process in acidic aqua solution, the polymerizing products are from dimer [1–4] to polymer with very high molar weight [5–11] under different conditions. The polymerizing products have also different structures from 0-D cluster anions to 1-D and 2-D subunits. The typical clusters are reported early, $\text{Mo}_6\text{O}_{19}^{2-}$ [12–15], $\text{Mo}_7\text{O}_{24}^{3-}$ [16,17], $\text{Mo}_8\text{O}_{26}^{4-}$ [15,18–21] and 1-D subunits may be simple chains constructed by MoO_6 octahedra [10,14,22–28], or consisting of $\text{Mo}_6\text{O}_{20}^{4-}$ or $\text{Mo}_8\text{O}_{26}^{4-}$ clusters by sharing edge of MoO_6 octahedra [8–10,21–25]. The reported 2-D subunits are $\{\text{Mo}_5\text{O}_{16}\}_\infty$ and $\{\text{Mo}_7\text{O}_{22}\}_\infty$ layers [17,23,29–31] constructed by $\{\text{Mo}_5\text{O}_{16}\}$ and $\{\text{Mo}_7\text{O}_{22}\}$ blocks via sharing the edges of MoO_6 octahedra.

A survey of the reported compounds shows that there are many factors influencing the components and structures of the polymeric products, such as reactants ratio [20,28] and sort of reactants [23], reaction temperature which impacts both the composition and topology of the Mo-POM blocks [23,32]. Even at same condition three products were isolated and carefully adjusting the pH could obtain the single product [33]. That is, in aqua solution the polymerizing reaction of molybdate anions is very complicated and several equilibria exist at the same time. Therefore reasonable selection of reactants and reaction conditions will help to obtain the target products. In this work, we chose 1,10-phen as organic component, molybdate and copper acetate as inorganic components to synthesize inorganic-organic hybrid of

polyoxomolybdate and the product, $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{Mo}_3\text{O}_{10}]$ (**1**), is a inorganic-organic supramolecular compound with Mo_3 -chain structure.

The asymmetric unit of **1** contains one $\{\text{Mo}_3\text{O}_{10}\}^{2-}$ (shortened as Mo_3) group, one Cu^{2+} ion, one phen ligand and two H_2O molecules (Fig. S1). The structure of **1** [34] may be described as a fishbone chain of edge-sharing $\{\text{MoO}_6\}$ octahedra, decorated with peripheral $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2]$ complex fragments as shown in Fig. 1. The coordination geometry of Cu^{2+} ion is defined by an apical water molecule and a basal plane generated by two nitrogen donors of the phen ligand, other water molecule and an oxo-group of $\{\text{Mo}_3\text{O}_{10}\}^{2-}$ group. The MoO_6 octahedra in **1** are all severely distorted with Mo—O bond lengths of 1.691(3) Å – 2.253(3) Å and O—Mo—O bond angles of 72.80(12)° – 104.66(14)° and 137.60(12)° – 166.67(12)° (Table S1). Each $\{\text{MoO}_6\}$ octahedron has four μ_3 -oxygen atoms and two terminal oxygen atoms, one of which bonds to Cu^{2+} ion. The $\{\text{MoO}_6\}$ octahedra are linked by edge-sharing into a straight chain along crystallographic *a*-axis. The complex fragments $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2]$ extend towards two sides of the chain so the chain may be described as a fish-bond one.

The fish-bond chains assemble in the form parallel each other (Fig. 2) so that a $\pi-\pi$ interaction is found between the phen rings belonging to two chains with some short C—C distances of 3.366 Å – 3.451 Å. On the other hand, between the chains there also exist hydrogen bonds (O2W—H2WB...O6 2.865 Å, O1W—H1WD...O8 2.862 Å) since the coordinated water molecules present in the complex fragments $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2]$ (Fig. 3). It is the hydrogen bonds and the $\pi-\pi$ interaction that construct the supramolecular compound (Fig. 4). In this compound the Mo_3 chain is same as that we reported early [18] but

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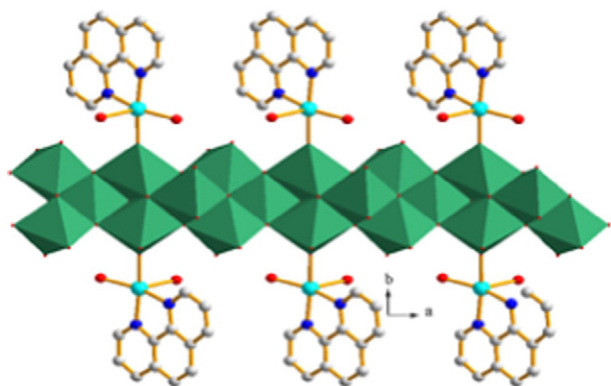


Fig. 1. Polyhedral and ball-stick representation of the fish-bond chain in **1**.

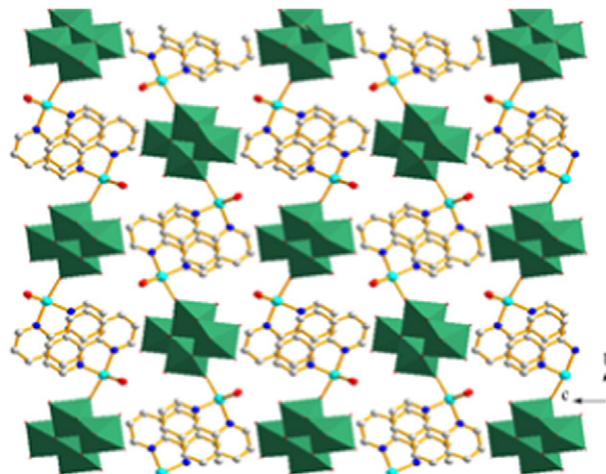


Fig. 4. Polyhedral and ball-stick representation of the chain stacking in **1**.

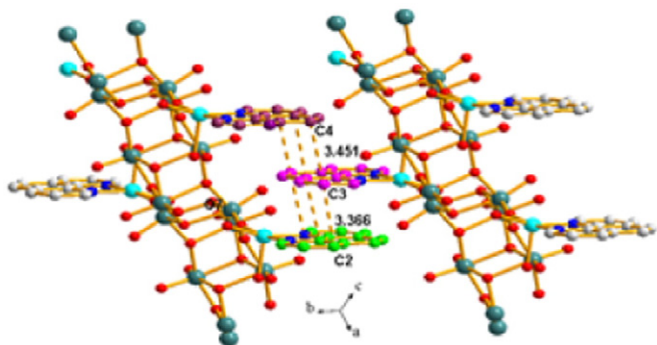


Fig. 2. π - π interaction between the phen rings belonging to two chains in **1**.

the crystal structure is very different with that in the oxidation number of copper and in dimension since the different organic ligands were used. Using a long bridging ligand gave a covalent three dimension structure and a chelating ligand leads to a chain structure, showing that the structure of the organic ligands greatly determine the structure of products.

The IR spectrum (Fig. S2) of **1** shows the vibration absorption bands of H₂O, CH bond of phen in 3372 cm⁻¹ and 3035 cm⁻¹, the bands of phen ring in 1100–1600 cm⁻¹ and bands of M–O bonds in 420–950 cm⁻¹. The bands at 490, 658 cm⁻¹, and 820, 887, 918, and 933 cm⁻¹ are assigned to $\nu(\text{Mo–O–Mo})$ and $\nu(\text{Mo=O})$, respectively [35].

The TG and DTA curves of **1** are shown in Fig. S3. The compound **1** is stable until to 220 °C, and then lost its coordination water molecules (obs. 5.3% and calc. 4.95%) accompanying an endothermic peak at 287 °C. After that in temperature range of 300–600 °C, phen underwent

a complicated decomposition process with four exothermic peaks at 366 °C, 394 °C, 430 °C and 470 °C. At 600 °C weight loss is 29.23%.

Phen is a good optical compound and used as analysis reagent in determination of metal ions. The photoluminescence property of compound **1** was investigated in the solid state at room temperature. Compound **1** exhibits a broad emission band centered at 500 nm (Fig. 5). Compared with the double emissions of free phen ($\lambda_{\text{em}} = 380$ nm (fluo) and 470–600 nm (phos) [36], the emission band of **1** should be assigned to the phosphorescent $n-\pi^*$ and $\pi-\pi^*$ transition from ligand-centered triple state according to Melnic's analysis [37] for the hard to oxidized metal ion Cu²⁺. The phosphorescence results from the coordination effect of phen to Cu²⁺ ion which increases the molecular rigidity and then changes the energy levels of phen as well intramolecular energy transfer.

The variable-temperature magnetic susceptibilities of newly prepared crystalline sample of **1** were measured from 2 to 300 K at a fixed field of 1000 Oe and are shown as plots of χ_m and $\chi_m T$ vs T (Fig. 6). The experiment $\chi_m T$ value of 0.79 cm³ K mol⁻¹ at 300 K is bigger than the calculated one ($\chi_m T = 0.125 g^2 \times 2 \times S(S+1) = 0.375$ cm³ K mol⁻¹, $g = 2.0$, $S = 1$ for only spinning contribution) for one Cu²⁺ ion. The $\chi_m T$ value decreases slowly to 0.377 cm³ K mol⁻¹ when the temperature decreases to 2 K, in agreement with the simple paramagnetic property of **1** derived from the crystal structure ($d_{\text{Cu...Cu}} = 7.634$ Å in the chain and 6.872 Å between the chains). The fitting to $1/\chi_m \sim T$ curve in 150 K–300 K (Fig. S4) shows that the compound **1** obeys the Curie law in this temperature range with $C = 1.076$ cm³·mol⁻¹ and $\theta = -104.5$ K. The bigger $\chi_m T$ value at 300 K is attributed to the spin-orbit coupling for the atom with more than five electrons in its d orbitals.

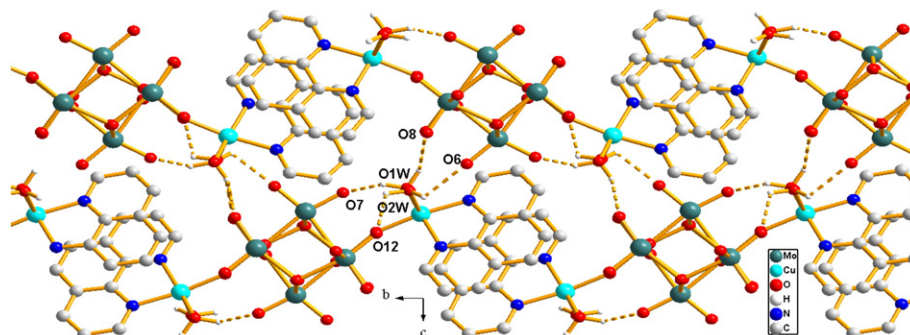


Fig. 3. Hydrogen bonds between the chains in **1**.

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